High Pressure Wide and Small Angle Scattering of Nanocrystals

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INTRODUCTION

Semiconductor nanocrystals are a class of materials which exhibit size dependent properties including the band gap, melting temperature and solid-solid phase transition pressure. Spherical nanocrystals with diameters of 1- 10 nm are nearly defect free, exhibit the same crystal structure as the bulk materials, and are dispersible in organic solvents because of the surfactant layer covering their surface which also prevents aggregation.

In the past, nanocrystals have been shown to demonstrate a size dependent transition pressure, and to transform coherently, preserving their defect free nature across the phase transition[1]. This latter quality is very different from the bulk in which pressure cycling generates more defects. The lack of defects make nanocrystals an ideal system for the study of phase transitions. In particular, what is the mechanism of the phase transition? How is this mechanism effected by the size of the particle? Nanocrystals can also be assembled in large arrays and superstructures with unknown and potentially interesting properties. To address these questions, we have undertaken an x-ray diffraction (XRD) study of large (diameter > 10 nm) nanocrystals and a small angle x-ray scattering (SAXS) study of 4 nm diameter particles under high pressure in a diamond anvil cell (DAC). Due to the extremely small sample volume (~ 1 nL) and the relative opacity of the diamonds, ranging from 10 % at 10 keV to 60 % at 20 keV, a synchrotron light source is necessary to carry out the experiment. This investigation represents the first complete high pressure experiment conducted at the Advanced Light Source.

EXPERIMENTAL

Nanocrystal preparation

Synthesis of the nanocrystals has been described in detail elsewhere[2]. Briefly, metal precursors of Cd and Se are injected quickly into hot (360 ^{o}C) surfactant, 90% n-tri-octylphosphene oxide (TOPO). Larger sizes were obtained by growing at 300^{o}C for long times (~ 1 day). Size distributions were 5 to 10 %. Sizes were determined by transmission electron microscopy and are in agreement with the diffraction patterns presented here.

High Pressure X-ray Diffraction

The high pressures necessary for this work are obtained in a diamond anvil cell (DAC). Nanocrystal powder is dissolved in ethylcyclohexane, a hydrostatic pressure medium, which is held in place between 500 μm culet diamonds with a spring steel gasket. Pressure is applied by mechanically pressing the two diamonds together and can reach 10 GPa in this cell. Pressure is determined by placing small chips of ruby and monitoring the pressure dependent florescence. Data was collected at ALS beamline 7.3.3 using monochromated x-rays in an angle dispersive geometry. For the XRD experiment, the wavelength was 0.76 Å and 1.11 Å for the SAXS experiment. Two-dimensional diffraction patterns are obtained with an x-ray CCD and

integrated over constant values of scattering angle, 2θ using the program FIT2D. An exponentially decaying background was fitted and subtracted from all XRD patterns shown here. Diffraction data is calibrated against LaB_6 (wide angle) and silver behenate (small angle) patterns collected in the DAC.

RESULTS AND DISCUSSION

X-ray Diffraction. A series of x-ray diffraction patterns at different pressures are shown in Fig. 1. The sample is raised from 0.7 GPa (A) to 9.1 GPa (B), then briefly reduced to atmospheric pressure and raised back to 1.4 GPa (C). At 0.7 GPa, the nanocrystals are in the wurtzite phase typical of CdSe. Note that the peaks are broadened with respect to the bulk, owing to Debye-Sherrer broadening which allows us to determine the size of the particles under consideration. Fitting with Guassian profiles (shown as solid lines) reveals an average domain size of 9.2 nm. At 9.1 GPa they have completely transformed to the rocksalt phase, with crystals showing a domain size of 6.0 nm. When the pressure is reduced to atmospheric, some of the crystals remain in the rocksalt phase as can be seen from the remaining (200) peak of rocksalt at $2\theta = 16^{o}$. Also, the apparent average crystallite size of the four coordinate (mixed wurtzite/zincblende) particles has regained its pre-transformation size of 9.2 nm. The rocksalt (200) peak has a domain size of 8.5 nm.

Interestingly, the apparent size of the domains decreases significantly across the transition then recovered to the pre-transformed domain size. This 35 % size change cannot be explained by the difference in crystal volume across the transition, which only accounts for a 14 % change. Furthermore, the nanocrystals are not fragmenting in the sense of becoming separate particles because after the transition they recover to the same size. The answer must lie in some sort of mechanism which breaks the nanocrystals into separate crystalline domains but then can be erased when the transition is reversed. For Debye-Sherrer broadening, the only condition necessary for this is that the crystalline domains not be oriented in the same direction. The mechanism which best explains the observed difference in domain sizes is as the nanocrystals transform, a twin defect is generated in the midst of the crystal. As shown in Fig 1(D), a twin defect is created when the boundary between two phases builds up strain in the crystal. At some point, this strain is sufficient to change the direction of travel of the phase boundary. This new direction will often have a well defined relation to the initial crystallite grain, forming a twin shown in Fig. 1(E). This definite relationship might provide the necessary condition for the nanocrystals to recover to a single coherent defect free domain.

The one remaining problem lies in the rocksalt peak which is still present in the recovered sample. This peak does not show the dimensions we would expect if it has transformed with a twin defect. Taking pressure differences into account, a 6.0 nm diameter rocksalt domain at 9.1 GPa would be 6.4 nm at 1.4 GPa. However, the problem can resolved by taking into consideration the size distribution of sample, which is about 5-10%. It is possible that the cross over size between forming a twin defect and transforming coherently is between 8 and 9 nm. Some percentage of the sample with smaller sizes would then not transform with a twin defect. These particles might also be more stable upon pressure release because they lack the defect.

Small Angle X-ray Scattering. Fig. 2 shows a pressure series taken at small angle for 4 nm diameter spheres at very high concentrations. The observed pattern is a consequence of multi-particle interactions and is very similar to that observed for nanocrystal colloid glasses[3]. It is quite possible that when pressure is applied the particles form into close-packed networks. As

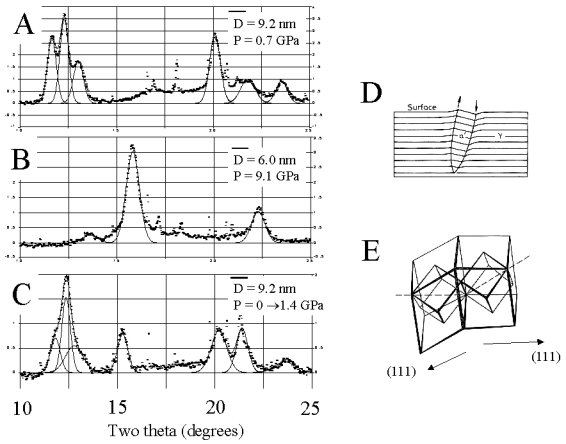

Figure 1. XRD pressure series (A-C) and model (D-E)

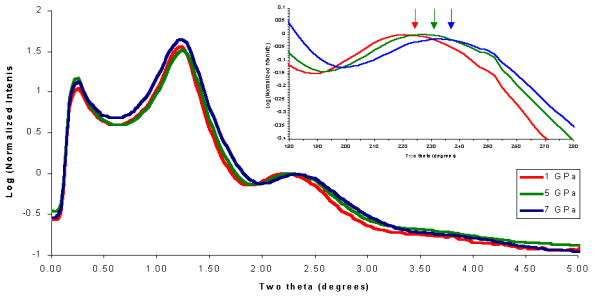

Figure 2. SAXS pressure series. Inset is blow-up of second peak. Arrows indicate peak position.

pressure is further applied, the primary peak does not noticeably shift, but the secondary peak does shift slightly as shown in the inset in Fig. 2. From 1 to 7 GPa, the secondary peak shifts from 2.25° to 2.38°. The shift to higher scattering angle is consistent with a shorter characteristic distance. Thus, the shift may be due to either the compression of the colloidal glass network or simply the compressibility of the individual nanocrystals. If the latter is true, the colloidal glasses would demonstrate a surprising degree of rigidity. The current experiment is, however, inconclusive. The relatively wide size distribution (5- 10 %) of the nanocrystals makes them form glasses rather than well defined colloidal crystals which would be give clearer data. It is also difficult to detect if the glass network changed appreciably across the phase transition of the constituent nanocrystals.

CONCLUSION

The analysis presented here is only preliminary, and will be done in greater detail. However, the results indicate that larger nanocrystals transform in a nature different from smaller nanocrystals, creating a twin defect which allows the recovered particles to regain their defect free nature. Furthermore, the high pressure properties of nanocrystal glasses and superlattices may prove that these materials have surprising resilient. Future experiments will focus on the extending the wide angle experiments to new materials (e.g. nanocrystalline oxides) and studying improved colloidal crystals, as well as across a greater pressure range.

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